REINFORCED CALCIUM ALUMINOSILICATE GLASS-CERAMICS

BACKGROUND OF THE INVENTION

U.S. Pat. No. 4,615,987 discloses the production of glass-ceramic articles, wherein the predominant crystal phase is selected from the group of anorthite, triclinic (CaO,SrO).Al_2O_3.2SiO_2, and its pseudo-binaries with mullite (3Al_2O_3.2SiO_2), cordierite (2MgO.2Al_2O_3.5SiO_2), barium osumilite (BaO.2MgO.3Al_2O_3.9SiO_2), albite solid solution ($Na_2O.Al_2O_3.6SiO_2$), gehlenite (2CaO.Al_2O_3.SiO_2), Al_2O_3, SiO_2, and CaO.SiO_2, reinforced through the entrainment therein of SiC fibers, SiC whiskers, or mixtures of SiC whiskers with fibers selected from the group of SiC, carbon, B_4C, BN, mullite, spinel, ZrO_2, zircon, glass, and Al_2O_3. In general, the reinforced composite articles exhibited use temperatures up to 1300° C. and utilized about 10–60% by volume SiC whiskers and/or 15–70% by volume fibers. The inclusion of whiskers imparted a substantial improvement in mechanical strength and a great enhancement in fracture toughness to the base glass-ceramics. The entrainment of fibers provided a great increase in mechanical strength and microcrack yield stress to the original glass-ceramics. The hybrid composite articles, i.e., the glass-ceramics containing both fibers and whiskers, evidenced significant improvements in the overall mechanical properties displayed by the articles. Of particular importance was the extraordinary increase in microcrack yield stress resulting from the combination of fibers and whiskers. The overall effect upon the other mechanical properties of the glass-ceramics generated by the combination of both fibers and whiskers was not as large as the sum of the two actions, but was considerably greater than the average of the two.

The glass-ceramics claimed in that patent were encompassed within the alkaline earth aluminosilicate system and consisted essentially, expressed in terms of weight percent on the oxide basis, of:

CaO	0–25	MgO	0–15
SrO	0–30	Na_2O	0–4
CaO + SrO	10–30	K_2O	0–6
Al_2O_3	25–38	TiO_2	0–12
SiO_2	35–60	ZrO_2	0–15
BaO	0–25	As_2O_3	0–3
BaO + MgO + Na_2O + K_2O + TiO_2 + ZrO_2 + As_2O_3			0–30

In general, a nucleation agent, e.g., TiO_2, was not included in the compositions but, instead, the precursor glass was comminuted to extremely finely-divided particles, normally to an average size smaller than 10 microns, and surface nucleation relied upon.

Further laboratory work has indicated that surface nucleation has several processing-related drawbacks. To illustrate:

The composites containing whiskers cannot be sintered into an integral body of substantial bulk exhibiting nearly full density at temperatures below the liquidus temperature for the composition. The composite may be sintered to dense bodies at temperatures above the liquidus temperature, but at such temperatures the desired crystalline assemblage cannot be developed because the multitudes of surfaces necessary for proper nucleation are no longer present. Consequently, such whisker-containing composites must generally be formed into articles through hot pressing or hot isostatic pressing below the liquidus temperature. Those methods of shaping articles are not only expensive, when compared to simple sintering, but also are limited in the type and complexity of the shapes that can be fabricated. For example, an extruded honeycomb structure cannot be formed through either of those processes.

Furthermore, fiber-containing composites currently prepared with surface nucleated compositions have been subject to unfavorable reliability with respect to crystallization. Thus, the parameters of the processing schedule are very critical and, if pressure is applied and compaction takes place prior to crystallization, the matrix will remain glassy with the desired high temperature properties of the final product deleteriously affected. Also, the temperature at which the composite article is consolidated must be carefully controlled to secure well-consolidated and well-crystallized composites.

We have found that glass-ceramic compositions containing nucleating agents, such that internal nucleation takes place, do not suffer from those shortcomings. Accordingly, sintering of whisker-reinforced composites may be undertaken at temperatures above the liquidus to insure the formation of an article of nearly full density, and, thereafter, the article is heat treated to effect crystallization in situ. Furthermore, the fabrication of composites containing fibers becomes substantially process insensitive and the glass-ceramic matrix more completely and uniformly crystallized when an internal nucleating agent is incorporated into the composition. That process insensitivity is of special importance in fabricating large, thick-walled parts where significant temperature gradients may be encountered. However, TiO_2, the traditional nucleating agent for converting aluminosilicate glasses into glass-ceramics, cannot be used with SiC fibers or whiskers since titanium silicide is formed which adversely affects the mechanical strength of the fibers and whiskers. Moreover, because composites exhibiting still higher use temperatures were sought, the fluxing action of TiO_2 must be avoided.

Therefore, the primary objectives of the present invention were two:

(1) to discover nucleating agents suitable for use with glass-ceramic bodies prepared from compositions in the alkaline earth aluminosilicate system to serve as matrices for SiC whiskers and/or fibers; and

(2) to develop glass-ceramic bodies in the alkaline earth aluminosilicate system exhibiting higher refractoriness than those claimed in U.S. Pat. No. 4,615,987.

Because the present invention is an improvement thereupon and because that patent details processes for the fabrication of alkaline earth aluminosilicate glass-ceramic articles containing SiC whiskers or SiC fibers, and hybrid composites containing both whiskers and fibers, the disclosure of that patent is incorporated herein in its entirety.

SUMMARY OF THE INVENTION

We have found a narrow range of compositions within the CaO'Al_2O_3'SiO_2 system, wherein Al_2O_3 is present in an amount which is at least 5 mole percent and can be up to 50 mole percent in excess of that present in triclinic anorthite, which compositions can be nucleated internally with a nucleating agent selected from the group consisting of Cr_2O_3, HfO_2, MoO_3,